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Microelements in Radon Waters of The Zaelsovsky field (The Southern Part of West Siberia)

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Abstract. The results of the studies of the mechanisms of microelements accumulation in the radon waters of the Zaelsovsky field (the southern part of West Siberia) are presented for the first time. The key role of the water-rock system in these processes is shown. The radon waters of calcium hydrocarbonate and calcium-sodium hydrocarbonate composition with total mineralization ranging from 322 up to 895 mg/dm³ (²²²Rn = 11-801 Bq/dm³) are prevailing in the field. Metal species such as Ag⁺, Ba²⁺, Zn²⁺, Ni²⁺, Mn²⁺, Sr²⁺, Fe²⁺ are represented by free ions, and Be²⁺, Fe³⁺, Zr⁴⁺, Ti⁴⁺ by hydroxide complexes. Calculations reveal that the waters are saturated with carbonate (modifications CaCO₃ and CaMg(CO₃)₂, MnCO₃, FeCO₃, PbCO₃), silicate ((Fe²⁺, Fe³⁺)₂ - 3Si₂O₅(OH)₄), hydroxide (FeOOH and MnOOH) and oxide minerals (modification SiO₂, TiO₂, Mn²⁺Mn³⁺O₄). Radon waters are unsaturated with some compounds of zircon, zinc, barium, molybdenum, iron, copper, strontium: ZrO₂, Zn(OH)₂, BaCO₃, CaMoO₄, FeMoO₄, CuO, CuMoO₄, Cu₃(NO₃)₂(OH)₂, Fe(OH)₂, Cu(OH)₂, SrSO₄, SrCO₃, 3MgO₂SiO₂·2H₂O etc. In some samples, the observed saturation of water is relatively rare phosphate minerals (Ca₁₀(PO₄)₆(OH)₂, Fe₃(PO₄)₂·8H₂O, MnHPO₄), chlorargyrite (AgCl) and lead molybdate (PbMoO₄). The concentrations of some elements (namely Sr, Pb, Zn Mo, Be) in the radon waters of the Zaelsovsky field are at the level of their concentrations in rocks.

1. Introduction

Radon waters have been under investigation for many decades [1-11]. The studies of the mechanisms responsible for the formation of the chemical composition of water are carried out; in particular, attention is paid to the microelemental composition. Novosibirsk is the only large city in Russia accommodating 12 proven deposits (regions) of radon waters for medical use at its territory and in the nearest neighborhood.

Prospecting works aimed at the search for radon waters were carried out within the years 1960-1980 by the hydrogeologists of the PGO Novosibirskgeologiya E.K. Verigo, N.K. Akhmetzhanova, B.L. Vrabiy, E.G. Kuksova, G.T. Kostenko, N.A. Plaksina, P.L. Makidon, L.N. Koss, V.A. Zhukovsky, I.P. Karpinsky and many others. The Zaelsovsky field is situated in the central part of Novosibirsk and is confined to the water-abundant regions of the north-western contact zone of the large Novosibirsk massif of upper Paleozoic granitoids which break through more ancient rocks of the Inya series of upper Devonian – lower Carboniferous age. The Paleozoic formations are overlaid by loose Quaternary sediments up to 50 m thick. They emerge at the day surface in some places in the high-water bed of the



Ob river. Similar hydrogeological conditions characterize the marginal areas of the West Siberian artesian basin [12-14].

The studies rely on the results of the analyses of 97 water samples and more than 1000 rock samples. Seven types (according to S.A. Shchukarev) of radon waters are developed at the Zaeltsovsky field; calcium hydrocarbonate and calcium-sodium hydrocarbonate waters with the total mineralization of 322 to 895 mg/dm³ are prevailing (Fig.1) [15]. The presence of radon in ground water is natural. Its content is provided by the occurrence of scattered radioactive minerals in granites and granodiorites. Radon (²²²Rn) content within the water-bearing zones of upper Devonian – lower Carboniferous hornstone and upper Paleozoic granites is 11 to 801 Bq/dm³.

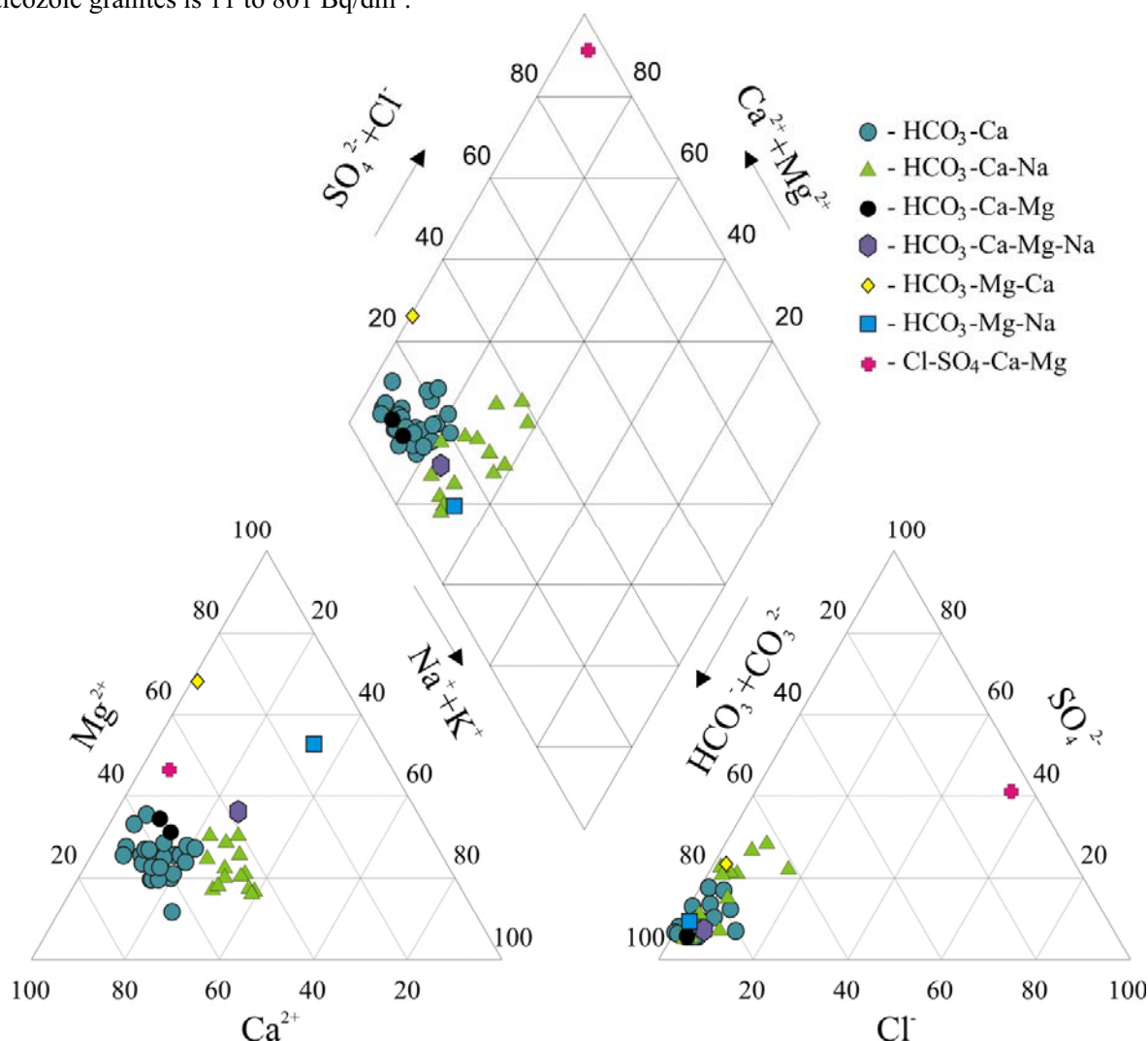


Figure 1. Piper diagram of the Zaeltsovsky.

Radon waters exhibit an interesting spectrum of microelement distribution (Fig. 2). One can see that the microcomponent composition of radon waters is characterized by increased content of Sr (up to 4,7 mg/dm³), Mn (up to 1,3 mg/dm³), and Ba (up to 0,2 mg/dm³). At the deposit, the concentration of silica in water varies within the range 7 to 36 mg/dm³. With an increase in total mineralization, in addition to Si, Sr, Mn and Ba other elements are accumulated in solution. Their concentrations are (µg/dm³): Cu (up to 13), Ag (up to 14), Mo (up to 31), Ni (up to 9,7), Zr (up to 52), Ti (up to 197), Pb (up to 78), Zn (up to

235), Co (up to 1,0), Li (up to 40) etc. Increased U content up to $98 \mu\text{g}/\text{dm}^3$ is characteristic of waters of the zone of upper Devonian – lower Carboniferous hornstone, while waters from the water-bearing zone of upper Paleozoic granites contain uranium at a level of $0,32\text{--}2,6 \mu\text{g}/\text{dm}^3$. Similar uranium concentration is also characteristic of the water from the Shivelig - 1 spring at the Shivelig field of radon water in the Republic of Tuva [16].

One of the major factors determining the chemical composition of water is the lithological conditions, namely the geological structure of the catchment, the chemical composition of rocks, and the relations between their types. A.I. Perelman proposed to evaluate the aqueous migration relying on the coefficient determined as a ratio of element content in the mineral residue of water to its content in rocks. This coefficient depicts the intensity of migration in water, determined by the properties of an element, and the degree of element concentrating or dissemination in water. The calculated coefficients of water migration formed a decreasing sequence: $\text{Mg}_{1429} > \text{Sr}_{92,2} > \text{Ti}_{35,16} > \text{P}_{30,38} > \text{Ba}_{15,9} > \text{Zn}_{2,64} > \text{Cr}_{1,23} > \text{Zr}_{0,96} > \text{U}_{0,86} > \text{Pb}_{0,53} > \text{Li}_{0,2} > \text{Ni}_{0,19} > \text{Cu}_{0,04} > \text{Co}_{0,03} > \text{Mo}_{0,01} > \text{Be}_{0,0004} > \text{Ag}_{0,000005}$.

The spectra of component distribution in the rocks and in water exhibit differentiation between the elements according to the coefficients of migration in water. The concentrations of some elements in the radon waters of the Zaeltsovsky field, namely Sr, Pb, Zn Mo, Be, are at the level of the concentrations in rocks (Fig.2) [16].

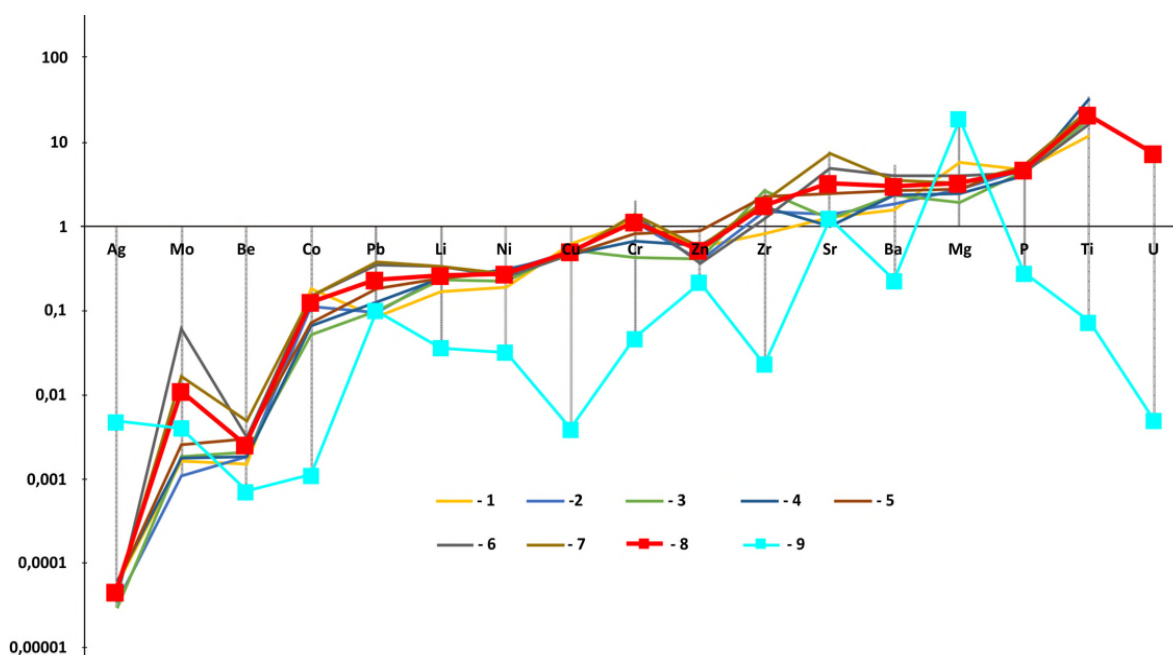


Figure 2. The spectra of microelement distribution in rocks and waters of the Zaeltsovsky field of radon waters. The distribution of microelements in the rocks of water-bearing horizons is: 1 - Q_{IV} , 2 - $a_3 Q_{III}$, 3 - $Q_{I-II} krd$, 4 - $P_3 nm$, 5 - D_3-C_1 , 6 - $D_3-C_1 + \gamma Pz_3$, 7 - γPz_3 , 8 - average. 9 – the average value of microelement content in radon waters.

For the first time, in the present work using the Visual Minteq, WATEQ4f and HG-32 software packages, we considered the scale of accumulation and the forms of microelement migration in radon waters, as well as the degree of the saturation of waters in the Zaeltsovsky field with various mineral phases.

Thus, the hydrogeochemical conditions of radon waters are responsible for the forms in which the microelements are present. The results of the thermodynamic modeling demonstrated that the forms of

cation migration in radon waters are free ions (>90%) and hydrocarbonate complexes (<10%). Alkaline (K^+ , Na^+ , Li^+) and alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) are present in the studied water entries in the form of monovalent (Me^+) and divalent (Me^{2+}) cations, respectively. Water saturation with oxygen causes rapid oxidation of Fe^{2+} into Fe^{3+} , so the compounds of iron (III) are more frequent in aqueous solutions because these compounds are thermodynamically more stable. Fe^{3+} is characterized by the ability to form stable complex compounds with some inorganic anions, especially with OH^- . For instance, the following hydro-oxide forms were identified in the studies of the major forms of Fe^{3+} migration: $Fe(OH)_2^+$, $(FeOH)_2^+$, $Fe(OH)_3$, $(Fe(OH)_4)^-$, $(Fe(OH)_2)^+$; the relations between these forms depend on pH and Eh of water, and on the total concentration of iron. Iron as Fe^{2+} migrates in the ion form, with the subordinate significance (1-7%) of sulfate complexes $FeSO_4(aq)$. A similar behavior is demonstrated by manganese, which migrates in the ion form Mn^{2+} (65-90%), and in the form of carbonate and sulfate complexes $MnCO_3(aq)$ (up to 4-23%) and $MnSO_4(aq)$ (1-5%).

The forms in which some microelements migrate will be considered below. Molybdenum migrates mainly in the form of a negatively charged oxide complex MoO_4^{2-} (59-67%), in smaller fractions as the complexes $MgMoO_4(aq)$ (14-22%) and $CaMoO_4(aq)$ (12-20%). Barium belongs to the elements of the small range of migration in water; it migrates mainly in the form of Ba^{2+} ion (>90%), complex hydrocarbonate ion $BaHCO_3^+$ and sulfate ion $BaSO_4(aq)$. Migration of a substantial fraction of beryllium (the element of the 1st group of danger) proceeds in the complex with hydroxide ion $Be(OH)_2(aq)$, as revealed in the water-accommodating rocks of the zones of upper Devonian – lower Carboniferous hornstone (D_3-C_1) and upper Paleozoic granites (γPz_3). The forms of silver occurrence are represented by free ions Ag^+ (39-65%), neutral aqua complexes $AgCl(aq)$ (0-55%) and negatively charged complex $AgCl_2^-$ (0,8-4,2 %). The major forms of lead and copper presence in radon waters are carbonate complexes $PbCO_3$ (79,8%) and $CuCO_3$ (80-91%). Zinc forms are represented mainly by free Zn^{2+} ions, to a smaller extent by carbonate complexes $ZnCO_3(aq)$ and hydrocarbonate complexes $ZnHCO_3$. The forms of uranium occurrence are represented mainly by the uranyl-carbonate complexes of calcium $Ca_2UO_2(CO_3)_3(aq)$ (61-75%) and $CaUO_2(CO_3)_3^{2-}$ (25-36%).

The studied radon waters are saturated or nearly equilibrium to the series of carbonates (calcite, dolomite, siderite, rhodochrosite, magnesite) and silicate minerals (greenalite, sepiolite), the minerals containing heavy metals in the lattice (manganite, barite, rhodochrosite, rutyl, tenorite) and iron hydroxides (ferrihydrite, goethite and other amorphous compounds), that is, these minerals precipitate from waters and cannot be the source of iron in waters. Under these conditions, active dissolution is exhibited by silicate minerals, chrysotile $Mg_3Si_2O_5(OH)_4$, sepiolite $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$, magnesite $MgCO_3$, strontianite $SrCO_3$, which are unstable under these conditions and act as the source of not only Mg but also Cu, Sr, Si, and other elements.

The features of the saturation of radon waters with respect to the minerals depending on their chemical composition were established. For example, HCO_3 -Ca waters are saturated with respect to calcite $CaCO_3$, ferrihydrite $FeOOH$, different modifications of SiO_2 , greenalite $(Fe^{2+}, Fe^{3+})_2 - 3Si_2O_5(OH)_4$, manganite $MnOOH$, rutile TiO_2 , siderite $FeCO_3$. The equilibrium with aragonite $CaCO_3$, chalcedony SiO_2 , cristobalite, dolomite, rhodochrosite and faterite is observed. Waters are unsaturated with respect to ZrO_2 , $Zn(OH)_2$, witherite $BaCO_3$, tenorite CuO , sepiolite $Mg_4(Si_6O_{15})(OH)_2 \cdot 6H_2O$, povellite $CaMoO_4$ and its modifications, pyrochroite $Mn^{2+}(OH)_2$, nesquehonite $MgCO_3 \cdot 3H_2O$, Na-jarosite $NaFe_3(SO_4)_2OH_6$, magnesite $MgCO_3$, ferrous molybdate $FeMoO_4$ and ferrous hydroxide $Fe(OH)_2$, epsomite $MgSO_4 \cdot 7H_2O$, celestine $SrSO_4$, brucite $Mg(OH)_2$, hypsum $CaSO_4 \cdot 2H_2O$ and anhydrite $CaSO_4$. Waters of the HCO_3 -Ca-Na composition are in equilibrium with respect to aragonite, barite $BaSO_4$, calcite $CaCO_3$, chlorargyrite $AgCl$, cerussite $PbCO_3$ and hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$, chalcedony, cristobalite, dolomite, siderite, faterite $CaCO_3$, $ZnCO_3$, and their deposition is probable in the case of the geochemical parameters of the medium (pH, Eh) change. The waters are saturated with ferrihydrite, greenalite, manganite, gausmannite, modifications of quartz, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, rhodochrosite $MnCO_3$ and rutile TiO_2 . The features of the microelement composition of separate samples of radon waters cause the formation and possible precipitation of a suspension containing such mineral phases as vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$, and

manganese hydrophosphate MnHPO_4 . However, radon waters are sharply unsaturated with respect to hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$.

Radon waters of the Zaeltsovskoe field are fissure, cold, with the 6-10 °C, occur at a depth of 50-200 m. The chemical composition of the waters (according to S.A. Shchukarev) is mainly calcium hydrocarbonate and calcium-sodium hydrocarbonate, with total mineralization 322-895 mg/dm³. All the wells drilled through granites and near-contact hornstone were tested for ²²²Rn content in water. Its concentrations vary within a broad range from 11 to 801 Bq/dm³, this means that these waters belong to low-radon and medium-radon with respect to ²²²Rn, mineral (according to the classification proposed by N.I. Tolstikhin). Radon concentration in water from the wells drilled through hornstone is 37-241 Bq/dm³. The content of ²³⁸U and ²²⁶Ra does not exceed 0.098 mg/dm³ and 1.9·10⁻⁹ mg/dm³, respectively.

The concentrations of some elements in the radon waters of the Zaeltsovsky field, namely Sr, Pb, Zn, Mo, Be are at the level of concentrations in rocks. The results of thermodynamic modeling showed that the forms of migration of the basic cations (K^+ , Na^+ , Li^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) in radon waters are free ions (>90%) and hydrocarbonate complexes (<10%). The forms of migration of Fe(III) are represented by $\text{Fe}(\text{OH})_2^+$, $(\text{FeOH})_2^+$, $\text{Fe}(\text{OH})_3$, $(\text{Fe}(\text{OH})_4)^-$, $(\text{Fe}(\text{OH})_2)^+$, while Fe^{2+} migrates in the ion form, with the subordinate significance (1-7%) of sulfate complexes $\text{FeSO}_4(\text{aq})$. Manganese exhibits a similar behavior migrating in the ion form Mn^{2+} (65-90%), as well as in the form of carbonate and sulfate complexes $\text{MnCO}_3(\text{aq})$ (up to 4-23%) and $\text{MnSO}_4(\text{aq})$ (1-5%). The major forms of lead and copper existence in radon waters are carbonate complexes PbCO_3 (79,8%) and CuCO_3 (80-91%). Zinc forms are represented mainly by free ions Zn^{2+} , to a lower extent by carbonate $\text{ZnCO}_3(\text{aq})$ and hydrocarbonate complexes ZnHCO_3 . The forms of uranium presence are represented mainly by uranyl-carbonate complexes of calcium $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ (61-75%) and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (25-36%).

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References

- [1] Alonso H, Cruz-Fuentes T, Rubiano J G, González-Guerra J, Cabrera M C, Arnedo M A, Tejera A, Rodríguez-Gonzalez A, Pérez-Torrado F J, Martel P 2015 Radon in Groundwater of the Northeastern Gran Canaria *Aquifer Water* 7 pp 2575-2590
- [2] Beitollahi M, Ghiassi-Nejad M, Esmaeli A, Dunker R 2007 Radiological studies in the hot spring region of Mahallat, central Iran *Radiat Prot Dosim* 123(4) pp 505-508
- [3] Bertolo, Bigliotto C 2004 Radon concentration in waters of geothermal Euganean basin-Veneto, Italy *Radiat Prot Dosim* 111(4) pp 355-358
- [4] Chaudhuri H, Nisith K D, Bhandari R K, Sen P, Sinh B 2010 Radon activity measurements around Bakreswar thermal springs *Radiat Meas* 45 pp 143-146
- [5] Duenas C, Fernandez M C, Enraquez C, Carretero J, Liger E 1998 Natural radioactivity levels in Andalusian spas *Water Res* 32(8) pp 2271-2278
- [6] Eross A, Madl-Szonyi J, Surbeck H, Horvath A, Goldscheider N, Csoma A E 2012 Radionuclides as natural tracers for the characterization of fluids in regional discharge areas, Buda Thermal Karst, Hungary *J. Hydrol.* 426-427 pp 124-137
- [7] Hoehn E, von Gunten H R 1989 Radon in Groundwater: A Tool to Assess Infiltration From Surface Waters to Aquifers *Water resources research* 25(8) pp 1795-1803
- [8] Kamenova-Totzeva R M, Kotova R M, Tenev J G, Totzev A V, Badulin V M 2015 Natural radioactivity content in Bulgarian drinking waters and consequent dose estimation *Radiat Prot Dosimetry* 164(3) pp 402-407
- [9] Kies A, Hengesch O, Tosheva Z, Nawrot A P, Jania J 2015 Overview on radon measurements in Arctic glacier waters *The Cryosphere Discuss* 9 pp 2013-2052

- [10] Santos T O, Bonotto D M 2014 ^{222}Rn , ^{226}Ra and hydrochemistry in the Bauru Aquifer System, São José do Rio Preto (SP), Brazil *Applied Radiation and Isotopes* 86 pp 109-117
- [11] Vinson D S, Vengosh A, Hirschfeld D, Dwyer G S 2009 Relationships between radium and radon occurrence and hydrochemistry in fresh groundwater from fractured crystalline rocks, North Carolina (USA) *Chemical Geology* 260 pp 159-171
- [12] Novikov D A 2017 Hydrogeochemistry of the Arctic areas of Siberian petroleum basins *Petroleum Exploration and Development* 44 pp 780-88
- [13] Novikov D A, Sukhorukova A F 2015 Hydrogeology of the northwestern margin of the West Siberian Artesian Basin *Arabian Journal of Geosciences* 8 pp 8703-8719
- [14] Novikov D A 2018 Genetic classification of subsurface waters and brines of Arctic regions of Siberia *IOP Conference Series: Earth and Environmental Science* 193(1) 012049
- [15] Sukhorukova A F, Novikov D A 2018 Hydrogeology of Zaeltsovsko-Mochishchensky manifestation of radon waters (Novosibirsk) XXII Meeting on Groundwaters of Siberia and the Far East with international participation 473-480
- [16] Bulatov A A, Kopylova Yu G, Dzhabarova N K, Rychkova K M, Arakchaa K D, Khvashchevskaya A A, Guseva N V, Pashagin A V 2013 New information on the composition of radon waters (Shiveligskoye field) Resort base and natural health-improving areas of Tuva and adjacent regions 1 pp 154-161
- [17] Korneeva T V, Novikov D A 2018 Mechanisms of accumulation of trace elements in the radon waters of the Zaeltsovskoye deposit (south of Western Siberia) XXII Meeting on Groundwaters of Siberia and the Far East with international participation pp 270-276